

CLAIMS

1. An electrochemical device component, comprising:
an active metal electrode having a first surface and a second surface;
a protective composite separator on the first surface of the electrode, the
5 composite comprising,
a first material layer in contact with the electrode, the first material
being ionically conductive and chemically compatible with the active metal;
and
a second material layer in contact with the first layer, the second
10 material being substantially impervious, ionically conductive and chemically
compatible with the first material;
wherein the ionic conductivity of the composite is at least 10^{-7} S/cm.
2. The component of claim 1, further comprising a current collector on the
second surface of the active metal electrode.
- 15 3. The component of claim 1, wherein the second material layer is the sole
electrolyte in a subsequently formed battery cell.
4. The component of claim 1, wherein the structure further comprises an
electrolyte.
5. The component of claim 1, wherein the ionic conductivity of the second
20 material layer is at least 10^{-7} S/cm
6. The component of claim 1, wherein the ionic conductivity of the second
material layer is between about 10^{-6} S/cm and 10^{-3} S/cm.
7. The component of claim 1, wherein the ionic conductivity of the second
material layer is about 10^{-3} S/cm.
- 25 8. The component of claim 1, wherein the thickness of the first material layer is
about 0.1 to 5 microns.
9. The component of claim 1, wherein the thickness of the first material layer is
about 0.2 to 1 micron.

10. The component of claim 1, wherein the thickness of the first material layer is about 0.25 micron.
11. The component of claim 1, wherein the thickness of the second material layer is about 0.1 to 1000 microns.
- 5 12. The component of claim 1, wherein the ionic conductivity of the second material layer is about 10^{-7} S/cm and the thickness of the second material layer is about 0.25 to 1 micron.
13. The component of claim 1, wherein the ionic conductivity of the second material layer is between about 10^{-4} about 10^{-3} S/cm and the thickness of the second material layer is about 10 to 500 microns.
- 10 14. The component of claim 13, wherein the thickness of the second material layer is about 10 to 100 microns.
- 15 15. The component of claim 1, wherein the active metal of the electrode is selected from the group consisting of alkali metals, alkaline earth metals, and transition metals.
16. The component of claim 1, wherein the active metal of the electrode is an alkali metal.
17. The component of claim 1, wherein the active metal of the electrode is lithium or a lithium alloy.
- 20 18. The component of claim 1, wherein the first layer comprises a material selected from the group consisting of active metal nitrides, active metal phosphides, and active metal halides, and active metal phosphorus oxynitride glass.
19. The component of claim 1, wherein the first layer comprises a material selected from the group consisting of Li_3N , Li_3P and LiI , LiBr , LiCl , LiF , and LiPON .
- 25 20. The component of claim 1, wherein the second layer comprises a material selected from the group consisting of phosphorus-based glass, oxide-based glass, sulphur-based glass, oxide/sulfide based glass, selenide based glass, gallium based glass, germanium based glass, glass-ceramic active metal ion conductors, sodium beta-alumina and lithium beta-alumina.

21. The component of claim 1, wherein the second layer comprises a material selected from the group consisting of LiPON, Li_3PO_4 , $\text{Li}_2\text{S} \cdot \text{SiS}_2$, $\text{Li}_2\text{S} \cdot \text{GeS}_2$, Ga_2S_3 , LISICON, NASICON, sodium and lithium beta-alumina.

22. The component of claim 1, wherein the first layer material comprises a
5 complex of an active metal halide and a polymer.

23. The component of claim 23, wherein the polymer is selected from the group consisting of poly(2-vinylpyridine), polyethylene and tetraalkylammonium.

24. The component of claim 23, wherein the complex is LiI-poly(2-vinylpyridine).

25. The component claim 1, wherein the first layer comprises Li_3N .

10 26. The component claim 1, wherein the first layer comprises Li_3P .

27. The component claim 1, wherein the first layer comprises LiPON.

28. The component of claim 1, wherein the second layer is an ion conductive glass-ceramic having the following composition:

Composition	mol %
P_2O_5	26-55%
SiO_2	0-15%
$\text{GeO}_2 + \text{TiO}_2$	25-50%
in which GeO_2	0--50%
TiO_2	0--50%
ZrO_2	0-10%
M_2O_3	$0 < 10\%$
Al_2O_3	0-15%
Ga_2O_3	0-15%
Li_2O	3-25%

15 and containing a predominant crystalline phase composed of $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from

the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga.

29. The component claim 28, wherein the first layer comprises Li_3P .

30. The component claim 28, wherein the first layer comprises Li_3N .

5 31. The component claim 28, wherein the first layer comprises $\text{LiI} \cdot \text{poly-2-vinylpyridine}$.

32. The component claim 28, wherein the first layer comprises LiPON .

33. The component of claim 1, wherein the second layer is a flexible membrane comprising particles of an ion conductive glass-ceramic having the following

10 composition:

Composition	mol %
P_2O_5	26-55%
SiO_2	0-15%
$\text{GeO}_2 + \text{TiO}_2$	25-50%
in which GeO_2	0--50%
TiO_2	0--50%
ZrO_2	0-10%
M_2O_3	$0 < 10\%$
Al_2O_3	0-15%
Ga_2O_3	0-15%
Li_2O	3-25%

and containing a predominant crystalline phase composed of $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga in a solid polymer electrolyte.

15

34. A protective composite battery separator, comprising:

an ionically conductive first material layer or precursor that is chemically compatible with an active metal and air; and

a second material layer in contact with the first layer, the second material
5 being substantially impervious, ionically conductive and chemically compatible with the first material;

wherein the ionic conductivity of the composite is at least 10^{-7} S/cm.

35. The separator of claim 34, wherein the ionic conductivity of the second material layer is about 10^{-4} to 10^{-3} S/cm.

10 36. The separator of claim 34, wherein the thickness of the first material layer is about 0.1 to 5 microns.

37. The separator of claim 34, wherein the thickness of the second material layer is about 0.1 to 1000 microns.

38. The separator of claim 34, wherein the ionic conductivity of the second
15 material layer is between about 10^{-4} to about 10^{-3} S/cm and the thickness of the second material layer is about 10 to 500 microns.

39. The separator of claim 38, wherein the thickness of the second material layer is about 10 to 100 microns

40. The separator of claim 34, wherein the first layer comprises LiPON.

20 41. The separator of claim 34, wherein the first layer comprises a metal nitride first layer material precursor.

42. The separator of claim 41, wherein the first layer comprises Cu_3N .

43. The separator of claim 34, wherein the second layer comprises a material
25 selected from the group consisting of substantially impervious phosphorus-based glass, oxide-based glass, sulphur-based glass, oxide/sulfide based glass, selenide based glass, gallium based glass, germanium based glass, and glass-ceramic active metal ion conductors, sodium beta-alumina and lithium beta-alumina.

44. The separator of claim 34, wherein the second layer comprises a material selected from the group consisting of LiPON, Li_3PO_4 , $\text{Li}_2\text{S} \cdot \text{SiS}_2$, $\text{Li}_2\text{S} \cdot \text{GeS}_2 \cdot \text{Ga}_2\text{S}_3$, LISICON, NASICON, sodium and lithium beta-alumina.

45. The separator of claim 34, wherein the second layer is an ion conductive glass-ceramic having the following composition:

Composition	mol %
P_2O_5	26-55%
SiO_2	0-15%
$\text{GeO}_2 + \text{TiO}_2$	25-50%
in which GeO_2	0--50%
TiO_2	0--50%
ZrO_2	0-10%
M_2O_3	$0 < 10\%$
Al_2O_3	0-15%
Ga_2O_3	0-15%
Li_2O	3-25%

and containing a predominant crystalline phase composed of $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga.

46. The separator of claim 34, wherein the second layer is a flexible membrane comprising particles of an ion conductive glass-ceramic having the following composition:

Composition	mol %
P_2O_5	26-55%
SiO_2	0-15%

GeO ₂ + TiO ₂	25-50%
in which GeO ₂	0--50%
TiO ₂	0--50%
ZrO ₂	0-10%
M ₂ O ₃	0 < 10%
Al ₂ O ₃	0-15%
Ga ₂ O ₃	0-15%
Li ₂ O	3-25%

and containing a predominant crystalline phase composed of Li_{1+x}(M,Al,Ga)_x(Ge_{1-y}Ti_y)_{2-x}(PO₄)₃ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and
5 Li_{1+x+y}Q_xTi_{2-x}Si_yP_{3-y}O₁₂ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga in a solid polymer electrolyte.

47. A method of fabricating an electrochemical device component, the method comprising:

forming a laminate of

10 an active metal anode,

a first material layer adjacent to the active metal anode that is ionically conductive and chemically compatible with an active metal, and

a second material layer adjacent to the first layer that is substantially impervious, ionically conductive and chemically compatible with the first material;

15 wherein the ionic conductivity of the composite is at least 10^{-7} S/cm.

48. The method of claim 47, wherein the forming of the laminate comprises:

(a) providing a substrate of one of an active metal anode and a layer of the second material;

(b) forming on the substrate a layer of the first material or a chemical precursor for the first material; and

(c) applying the other of the active metal anode and the layer of the second material from (a) to the layer of the first material or precursor on the substrate.

5 49. The method of claim 48, wherein the active metal of the anode is lithium or a lithium alloy.

50. The method of claim 48, wherein the first material and precursors are selected from the group consisting of active metal nitrides, active metal phosphides, active metal halides, active metal phosphorus oxynitride glass, a complex of an active metal
10 halide and a polymer, metal nitrides, red phosphorus, amines, phosphines, borazine ($B_3N_3H_6$), triazine ($C_3N_3H_3$) and halides.

51. The method of claim 48, wherein the second material is selected from the group consisting of substantially impervious phosphorus-based glass, oxide-based glass, sulphur-based glass, oxide/sulfide based glass, selenide based glass, gallium
15 based glass, germanium based glass, glass-ceramic active metal ion conductors, sodium beta-alumina and lithium beta-alumina.

52. The method of claim 48, wherein the second layer is an ion conductive glass-ceramic having the following composition:

Composition	mol %
P_2O_5	26-55%
SiO_2	0-15%
$GeO_2 + TiO_2$	25-50%
in which GeO_2	0--50%
TiO_2	0--50%
ZrO_2	0-10%
M_2O_3	$0 < 10\%$
Al_2O_3	0-15%
Ga_2O_3	0-15%

Li ₂ O	3-25%
-------------------	-------

- and containing a predominant crystalline phase composed of Li_{1+x}(M,Al,Ga)_x(Ge_{1-y}Ti_y)_{2-x}(PO₄)₃ where X≤0.8 and 0≤Y≤1.0, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and
- 5 Li_{1+x+y}Q_xTi_{2-x}Si_yP_{3-y}O₁₂ where 0<X≤0.4 and 0<Y≤0.6, and where Q is Al or Ga.

53. The method of claim 48, wherein the second layer is a flexible membrane comprising particles of an ion conductive glass-ceramic having the following composition:

Composition	mol %
P ₂ O ₅	26-55%
SiO ₂	0-15%
GeO ₂ + TiO ₂	25-50%
in which GeO ₂	0--50%
TiO ₂	0--50%
ZrO ₂	0-10%
M ₂ O ₃	0 < 10%
Al ₂ O ₃	0-15%
Ga ₂ O ₃	0-15%
Li ₂ O	3-25%

- 10 and containing a predominant crystalline phase composed of Li_{1+x}(M,Al,Ga)_x(Ge_{1-y}Ti_y)_{2-x}(PO₄)₃ where X≤0.8 and 0≤Y≤1.0, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and Li_{1+x+y}Q_xTi_{2-x}Si_yP_{3-y}O₁₂ where 0<X≤0.4 and 0<Y≤0.6, and where Q is Al or Ga in a solid polymer electrolyte.

- 15 54. The method of claim 48, wherein the substrate is the second material layer, the first material or precursor layer is a first material layer selected from the group

consisting of active metal nitrides, active metal phosphides, active metal halides, and the active metal anode is lithium deposited by evaporation.

55. The method of claim 48, wherein the substrate is the second material layer, the first material or precursor layer is a precursor selected from the group consisting of
 5 metal nitrides, red phosphorus, amines, phosphines, borazine ($B_3N_3H_6$), triazine ($C_3N_3H_3$) and halides, and the active metal anode is lithium deposited by evaporation, whereby the precursor is converted to its lithiated first layer material analog by reaction with lithium during the evaporation deposition.

56. The method of claim 48, wherein the substrate is the second material layer, the
 10 first material or precursor layer is LiPON, and the active metal anode is lithium deposited by evaporation on a transient layer formed on the LiPON prior to lithium deposition, whereby the transient layer prevents reaction between vapor phase lithium and the LiPON.

57. The method of claim 56, wherein the transient layer comprises a metal
 15 miscible in lithium.

58. The method of claim 57, wherein the metal is Ag.

59. The method of claim 48, wherein the substrate is the second material layer and the first material or precursor layer is a LiI-poly(2-vinylpyridine) complex formed by application of a poly(2-vinylpyridine) to the second material layer, followed by
 20 application of iodine to the poly(2-vinylpyridine), followed by application of lithium as the active metal anode, whereby the LiI-poly(2-vinylpyridine) complex is formed.

60. The method of claim 59, wherein the active metal anode is applied by evaporation of lithium.

61. The method of claim 59, wherein the active metal anode is applied as a lithium
 25 foil.

62. A battery cell, comprising:

an active metal negative electrode having a first surface and a second surface;

a composite separator on the first surface of the electrode, the composite comprising,

a first material layer in contact with the electrode that is ionically conductive and chemically compatible with an active metal; and

a second material layer in contact with the first layer, the second material being, substantially impervious, ionically conductive and chemically compatible with the first material,

wherein the ionic conductivity of the composite is at least 10^{-7} S/cm; and

a positive electrode chosen from a sulfur-based positive electrode, a metal oxide based positive electrode, and a metal sulfide based positive electrode in contact with said second layer.

63. The battery cell of claim 62, further comprising a polymer electrolyte between the two electrodes.

64. The battery cell of claim 62, wherein the active metal of the negative electrode is lithium or a lithium alloy.

65. The battery cell of claim 62, wherein the first layer comprises a material selected from the group consisting of active metal nitrides, active metal phosphides, and active metal halides, and active metal phosphorus oxynitride glass.

66. The battery cell of claim 62, wherein the first layer comprises a material selected from the group consisting of Li_3N , Li_3P and LiI , LiBr , LiCl , LiF , and LiPON .

67. The battery cell of claim 62, wherein the first layer material comprises a complex of an active metal halide and a polymer.

68. The battery cell of claim 67, wherein the complex is LiI -poly(2-vinylpyridine).

69. The battery cell of claim 62, wherein the second layer comprises a material selected from the group consisting of phosphorus-based glass, oxide-based glass, sulphur-based glass, oxide/sulfide based glass, selenide based glass, gallium based glass, germanium based glass, glass-ceramic active metal ion conductors, sodium beta-alumina and lithium beta-alumina.

70. The battery cell of claim 62, wherein the second layer is an ion conductive glass-ceramic having the following composition:

Composition	mol %
-------------	-------

P ₂ O ₅	26-55%
SiO ₂	0-15%
GeO ₂ + TiO ₂	25-50%
in which GeO ₂	0--50%
TiO ₂	0--50%
ZrO ₂	0-10%
M ₂ O ₃	0 < 10%
Al ₂ O ₃	0-15%
Ga ₂ O ₃	0-15%
Li ₂ O	3-25%

- and containing a predominant crystalline phase composed of $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and
- 5 $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga.

71. The battery cell of claim 62, wherein the second layer is a flexible membrane comprising particles of an ion conductive glass-ceramic having the following composition:

Composition	mol %
P ₂ O ₅	26-55%
SiO ₂	0-15%
GeO ₂ + TiO ₂	25-50%
in which GeO ₂	0--50%
TiO ₂	0--50%
ZrO ₂	0-10%
M ₂ O ₃	0 < 10%

Al_2O_3	0-15%
Ga_2O_3	0-15%
Li_2O	3-25%

and containing a predominant crystalline phase composed of $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and
 5 $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga in a solid polymer electrolyte.

72. A method of making a battery cell, comprising:

forming a laminate of

an active metal electrode,

10 a first material layer in contact with the electrode, the first material being ionically conductive and chemically compatible with the active metal, and

a second material layer in contact with the first layer, the second material being substantially impervious, ionically conductive and chemically
 15 compatible with the first material,

wherein the ionic conductivity of the composite is at least 10^{-7} S/cm; and

applying a positive electrode chosen from a sulfur-based positive electrode, a metal oxide based positive electrode, and a metal sulfide based positive electrode in contact with said second material layer.

20